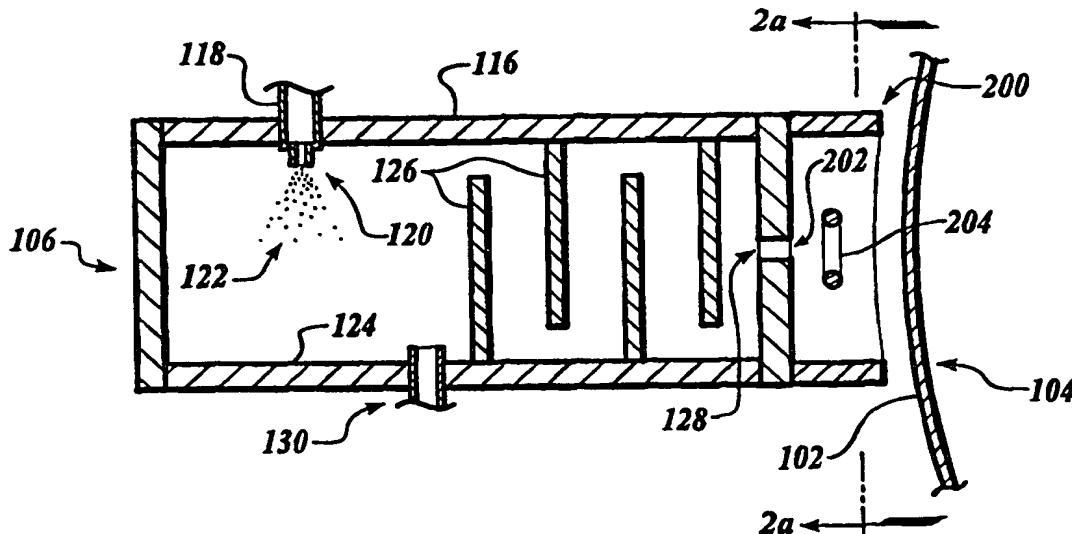




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(54) Title: METHOD OF MAKING LIGHT EMITTING POLYMER COMPOSITE MATERIAL



(57) Abstract

The method of the present invention for making a light emitting polymer has the steps of: a) flash evaporating a coating material monomer together with light emitting particles in an evaporate outlet forming an evaporate; b) cryocondensing the evaporate; and c) crosslinking the condensed evaporate. The evaporate may be passed to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; then d) cryocondensing the glow discharge monomer plasma on the surface and crosslinking the glow discharge monomer plasma thereon, wherein the crosslinking results from radicals created in the glow discharge monomer plasma and achieves self curing.

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METHOD OF MAKING LIGHT EMITTING POLYMER COMPOSITE MATERIAL

5

FIELD OF THE INVENTION

The present invention relates generally to a method of making composite polymer films. More specifically, the present invention relates to making a 10 composite polymer film from a mixture having insoluble particles in a liquid monomer. Additional layers of polymer or metal may be added under vacuum as well.

As used herein, the term "(meth)acrylic" is defined as "acrylic or methacrylic". Also, "(meth)acrylate" is defined as "acrylate or methacrylate".

15 As used herein, the term "cryocondense" and forms thereof refers to the physical phenomenon of a phase change from a gas phase to a liquid phase upon the gas contacting a surface having a temperature lower than a dew point of the gas.

20 As used herein, the term "conjugated" refers to a chemical structure of alternating single and double bonds between carbon atoms in a carbon atom chain.

25 As used herein, the term "composite polymer" is a polymer having two distinct phases wherein a first phase is substantially continuous and encompasses "islands" of a second phase from the molecular level to molecular aggregate level. The "islands" of the second phase may touch and/or the two phases may be unlinked or linked, but do not provide a continuous conjugated network. Hence, any conjugation present in the composite polymer is insufficient to render the composite polymer electrically conductive even in the presence of a dopant (iodine or salt).

30

BACKGROUND OF THE INVENTION

The basic process of plasma enhanced chemical vapor deposition (PECVD) is described in THIN FILM PROCESSES, J.L. Vossen, W. Kern, editors, Academic Press, 1978, Part IV, Chapter IV - 1 Plasma Deposition of Inorganic Compounds, Chapter IV - 2 Glow Discharge Polymerization, herein incorporated by reference. Briefly, a glow discharge plasma is generated on an electrode that may be smooth or have pointed projections. Traditionally, a gas inlet introduces high vapor pressure monomeric gases into the plasma region wherein radicals are formed so that upon subsequent collisions with the substrate, some of the radicals in the monomers chemically bond or cross link (cure) on the substrate. The high vapor pressure monomeric gases include gases of CH₄, SiH₄, C₂H₆, C₂H₂, or gases generated from high vapor pressure liquid, for example styrene (10 torr at 87.4 EF (30.8 EC)), hexane (100 torr at 10.4 EF (15.8 EC)), tetramethyldisiloxane (10 torr at 82.9 EF (28.3 EC) 1,3,-dichlorotetra-methyldisiloxane) and combinations thereof that may be evaporated with mild controlled heating. Because these high vapor pressure monomeric gases do not readily cryocondense at ambient or elevated temperatures, deposition rates are low (a few tenths of micrometer/min maximum) relying on radicals chemically bonding to the surface of interest instead of cryocondensation. Remission due to etching of the surface of interest by the plasma competes with reactive deposition. Lower vapor pressure species have not been used in PECVD because heating the higher molecular weight monomers to a temperature sufficient to vaporize them generally causes a reaction prior to vaporization, or metering of the gas becomes difficult to control, either of which is inoperative.

The basic process of flash evaporation is described in U.S. patent 4,954,371 herein incorporated by reference. This basic process may also be referred to as polymer multi-layer (PML) flash evaporation. Briefly, a radiation polymerizable and/or cross linkable material is supplied at a temperature below a decomposition temperature and polymerization temperature of the material. The material is atomized to droplets having a droplet size ranging from about 1 to

about 50 microns. An ultrasonic atomizer is generally used. The droplets are then flash vaporized, under vacuum, by contact with a heated surface above the boiling point of the material, but below the temperature which would cause pyrolysis. The vapor is cryocondensed on a substrate then radiation 5 polymerized or cross linked as a very thin polymer layer.

According to the state of the art of making plasma polymerized films, PECVD and flash evaporation or glow discharge plasma deposition and flash evaporation have not been used in combination. However, plasma treatment of a substrate using glow discharge plasma generator with inorganic compounds 10 has been used in combination with flash evaporation under a low pressure (vacuum) atmosphere as reported in J.D. Affinito, M.E. Gross, C.A.. Coronado, and P.M. Martin, AVacuum Deposition Of Polymer Electrolytes On Flexible Substrates. "Paper for Plenary talk in A Proceedings of the Ninth International Conference on Vacuum Web Coating", November 1995 ed R. Bakish, Bakish Press 1995, pg 20-36., and as shown in FIG. 1a. In that system, the plasma 15 generator 100 is used to etch the surface 102 of a moving substrate 104 in preparation to receive the monomeric gaseous output from the flash evaporation 106 that cryocondenses on the etched surface 102 and is then passed by a first curing station (not shown), for example electron beam or ultra-violet radiation, to 20 initiate cross linking and curing. The plasma generator 100 has a housing 108 with a gas inlet 110. The gas may be oxygen, nitrogen, water or an inert gas, for example argon, or combinations thereof. Internally, an electrode 112 that is smooth or having one or more pointed projections 114 produces a glow discharge and makes a plasma with the gas which etches the surface 102. The 25 flash evaporator 106 has a housing 116, with a monomer inlet 118 and an atomizing nozzle 120, for example an ultrasonic atomizer. Flow through the nozzle 120 is atomized into particles or droplets 122 which strike the heated surface 124 whereupon the particles or droplets 122 are flash evaporated into a gas that flows past a series of baffles 126 (optional) to an outlet 128 and 30 cryocondenses on the surface 102. Although other gas flow distribution arrangements have been used, it has been found that the baffles 126 provide adequate gas flow distribution or uniformity while permitting ease of scaling up to

large surfaces 102. A curing station (not shown) is located downstream of the flash evaporator 106. The monomer may be an (meth)acrylate (FIG. 1b).

Organic light emitting devices (OLED) may be long chain conjugated polymers with molecular weights on the order of 10^5 dalton, or small molecules, for example, aluminum quinolinolato, quinacridone or triphenyl diamine derivative. Fabrication of OLED with small molecules has been with (1) conventional electron beam or thermal, evaporation or sublimation of a solid small molecule material from a crucible; (2) spin coating of the small molecule material suspended in a solution of solvent and a polymeric binder followed by removal of the solvent; and (3) spin coating as for (2) but with a polymeric electrolyte binder. The evaporation/sublimation methods produce a film that is substantially composed of the light emitting small molecule. These methods offer high deposition rates, and other advantages, but suffer from the disadvantage of the difficulty of evaporating the small molecule material without significant thermal degradation. In spin coating, the film produced is a composite of a molecularly doped polymer (MDP) wherein the small molecules are dispersed throughout either a polymer or electrolyte. The difficulty is controlling thickness in the few hundred angstrom range necessary to control turn-on voltage.

Hence, there is a need for a method of making MDP at a high deposition rate, without thermal degradation and with controlled thickness at any thickness including the few hundred angstrom range.

SUMMARY OF THE INVENTION

The present invention is a method of making a first solid composite polymer layer of polymer doped with light emitting material. The method has the steps of (a) flash evaporating a coating monomer together with light emitting material forming an evaporate; (b) cyrocondensing the evaporate onto a surface; and (c) crosslinking condensed evaporate. The evaporate may be passed to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; then (d) cryocondensing the glow discharge monomer plasma on a surface whereupon condensed glow

discharge plasma as a liquid begins crosslinking. The crosslinking results from radicals created in the glow discharge plasma and achieves self curing.

It is, therefore, an object of the present invention to provide a method of making a composite polymer of polymer with light emitting material via flash evaporation.

An advantage is that the conjugation (if any) is preserved during curing. Another advantage of the present invention is that multiple layers of materials may be combined. For example, as recited in U.S. patents 5,547,508 and 5,395,644, 5,260,095, hereby incorporated by reference, multiple polymer layers, 10 alternating layers of polymer and metal, and other layers may be made with the present invention in the vacuum environment.

An advantage of the present invention using plasma curing is insensitivity to a direction of motion of the substrate because the deposited monomer layer is self curing. Because of rapid self curing, the monomer has 15 less time to flow and is therefore more uniformly thick. A further advantage is that the conjugation (if any) is preserved during curing.

The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both the organization and method of operation, together with further advantages and 20 objects thereof, may best be understood by reference to the following detailed description in combination with the drawings wherein like reference characters refer to like elements.

BRIEF DESCRIPTION OF THE DRAWINGS

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FIG. 1a is a cross section of a prior art combination of a glow discharge plasma generator with inorganic compounds with flash evaporation.

FIG. 1b is a chemical diagram of (meth)acrylate.

FIG. 1c is a chemical diagram of phenylacetylene.

30

FIG. 1d is a chemical diagram of triphenyl diamine derivitive.

FIG. 1e is a chemical diagram of quinacridone.

FIG. 1f is a chemical diagram of aluminum quinolinolato

FIG. 2 is a cross section of the apparatus of the present invention of combined flash evaporation and glow discharge plasma deposition.

FIG. 2a is a cross section end view of the apparatus of the present invention.

5 FIG. 3 is a cross section of the present invention wherein the substrate is the electrode.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

10 According to the present invention, a first solid polymer composite layer is made by the steps of:

- (a) mixing a liquid monomer with light emitting particles substantially insoluble in the liquid monomer forming a monomer particle mixture;
- (b) flash evaporating the monomer particle mixture forming a composite vapor; and
- 15 (c) continuously cryocondensing the composite vapor on a cool substrate and cross linking a cryocondensed monomer layer thereby forming the composite polymer layer.

Flash evaporation has the steps:

- 20 (a) supplying a continuous liquid flow of the monomer particle mixture into a vacuum environment at a temperature below both the decomposition temperature and the polymerization temperature of the monomer particle mixture;
- (b) continuously atomizing the monomer particle mixture into a continuous flow of droplets;
- 25 (c) continuously vaporizing the droplets by continuously contacting the droplets on a heated surface having a temperature at or above a boiling point of the liquid monomer and of the particles, but below a pyrolysis temperature, forming a composite vapor.

30 The light emitting organic molecules are introduced to the monomer as particles. During flash evaporation, both the monomer and the particles are vaporized. As a result of this vaporization, the light emitting organic molecules

are then dispersed among the monomer molecules whereupon condensation or cryocondensation, the composite is formed wherein the light emitting organic molecules are distributed within the composite at a molecular level. In other words, the light emitting organic molecules are dispersed in a polymeric matrix.

5 Insoluble is defined as not dissolving. Substantially insoluble refers to any amount of a particle material not dissolved in the liquid monomer. Examples include solid particles that are insoluble or partially soluble in the liquid monomer, immiscible liquids that are fully or partially miscible/insoluble in the liquid monomer, and dissolvable solids that have a concentration greater than the 10 solubility limit of the monomer so that an amount of the dissolvable solid remains undissolved.

15 The insoluble particles are preferably of a volume much less than about 5000 cubic micrometers (diameter about 21 micrometers) or equal thereto, preferably less than or equal to about 4 cubic micrometers (diameter about 2 micrometers). In a preferred embodiment, the insoluble particles are sufficiently small with respect to particle density and liquid monomer density and viscosity 20 that the settling rate of the particles within the liquid monomer is several times greater than the amount of time to transport a portion of the particle liquid monomer mixture from a reservoir to the atomization nozzle. It is to be noted that it may be necessary to stir the particle liquid monomer mixture in the reservoir to maintain suspension of the particles and avoid settling.

25 Upon spraying, the droplets may be particles alone, particles surrounded by liquid monomer and liquid monomer alone. Since both the liquid monomer and the particles are evaporated, it is of no consequence either way. It is, however, important that the droplets be sufficiently small that they are completely vaporized. Accordingly, in a preferred embodiment, the droplet size may range from about 1 micrometer to about 50 micrometers.

30 After condensation, the cross linking may be by radiation curing or by self curing. In radiation curing (FIG. 1), the monomer liquid may include a photoinitiator. In self curing, a combined flash evaporator, glow discharge plasma generator is used without either the e-beam gun or ultraviolet light.

The mixture of monomer and insoluble or partially soluble particles may be considered a slurry, suspension or emulsion, and the particles may be solid or liquid. The mixture may be obtained by several methods. One method is to mix insoluble particles of a specified size into the monomer. The insoluble particles 5 of a solid of a specified size may be obtained by direct purchase or by making them by one of any standard techniques, including but not limited to milling from large particles, precipitation from solution, melting/spraying under controlled atmospheres, rapid thermal decomposition of precursors from solution as described in U.S. patent 5,652,192 hereby incorporated by reference. The steps 10 of U.S. patent 5,652,192 are making a solution of a soluble precursor in a solvent and flowing the solution through a reaction vessel, pressurizing and heating the flowing solution and forming substantially insoluble particles, then quenching the heated flowing solution and arresting growth of the particles. Alternatively, larger sizes of solid material may be mixed into liquid monomer then agitated, for 15 example ultrasonically, to break the solid material into particles of sufficient size.

Liquid particles may be obtained by mixing an immiscible liquid with the monomer liquid and agitating by ultrasonic or mechanical mixing to produce liquid particles within the liquid monomer. Immiscible liquids include, for example phenylacetylene.

20 The liquid monomer may be any liquid monomer useful in flash evaporation for making polymer films. Liquid monomer includes but is not limited to meth(acrylate) monomer, for example tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate, caprolactone acrylate and combinations thereof; methacrylate monomers; and combinations 25 thereof. The (meth)acrylate monomers are particularly useful in making light emitting polymers (LEP).

30 The insoluble light emitting particle may be any insoluble or partially insoluble particle type having a boiling point below a temperature of the heated surface in the flash evaporation process. Insoluble light emitting particle includes but is not limited to conjugated material for example triphenyl diamine derivative (TPD, FIG. 1d), quinacridone (QA, FIG. 1e), aluminum quinolinolato (Alq, FIG. 1f) and combinations thereof.

To achieve a light emitting composite, the insoluble particles may be on a molecular level within the matrix as a molecularly doped polymer (MDP) or may be multi-molecule particles within the matrix.

Making an LEP is done with the apparatus shown in FIG. 2. The apparatus and method of the present invention are preferably within a low pressure (vacuum) environment or chamber. Pressures preferably range from about 10^{-1} torr to 10^{-6} torr. The flash evaporator 106 has a housing 116, with a monomer inlet 118 and an atomizing nozzle 120. Flow through the nozzle 120 is atomized into particles or droplets 122 which strike the heated surface 124 whereupon the particles or droplets 122 are flash evaporated into a gas or evaporate that flows past a series of baffles 126 to an evaporate outlet 128 and cryocondenses on the surface 102. Cryocondensation on the baffles 126 and other internal surfaces is prevented by heating the baffles 126 and other surfaces to a temperature in excess of a cryocondensation temperature or dew point of the evaporate. Although other gas flow distribution arrangements have been used, it has been found that the baffles 126 provide adequate gas flow distribution or uniformity while permitting ease of scaling up to large surfaces 102. Crosslinking is by radiation curing.

In another embodiment, the evaporate outlet 128 directs gas toward a glow discharge electrode 204 creating a glow discharge plasma from the evaporate. In the embodiment shown in FIG. 2, the glow discharge electrode 204 is placed in a glow discharge housing 200 having an evaporate inlet 202 proximate the evaporate outlet 128. In this embodiment, the glow discharge housing 200 and the glow discharge electrode 204 are maintained at a temperature above a dew point of the evaporate. The glow discharge plasma exits the glow discharge housing 200 and cryocondenses on the surface 102 of the substrate 104.

In either embodiment, it is preferred that the substrate 104 is kept at a temperature below a dew point of the evaporate, preferably ambient temperature or cooled below ambient temperature to enhance the cryocondensation rate. In these embodiments, the substrate 104 is moving and may be electrically grounded, electrically floating or electrically biased.

Where glow discharge is used, and If the substrate **104** is electrically biased, it may even replace the electrode **204** and be, itself, the electrode which creates the glow discharge plasma from the monomer gas. Substantially not electrically biased means that there is no impressed voltage although a charge 5 may build up due to static electricity or due to interaction with the plasma. A preferred shape of the glow discharge electrode **204**, is shown in FIG. 2a. In this preferred embodiment, the glow discharge electrode **204** is separate from the substrate **104** and shaped so that evaporate flow from the evaporate inlet **202** substantially flows through an electrode opening **206**. Any electrode shape can 10 be used to create the glow discharge, however, the preferred shape of the electrode **204** does not shadow the plasma from the evaporate issuing from the outlet **202** and its symmetry, relative to the monomer exit slit **202** and substrate **104**, provides uniformity of the evaporate vapor flow to the plasma across the width of the substrate while uniformity transverse to the width follows from the 15 substrate motion.

The spacing of the electrode **204** from the substrate **104** is a gap or distance that permits the plasma to impinge upon the substrate. This distance that the plasma extends from the electrode will depend on the evaporate species, electrode **204**/ substrate **104** geometry, electrical voltage and 20 frequency, and pressure in the standard way as described in detail in ELECTRICAL DISCHARGES IN GASSES, F.M. Penning, Gordon and Breach Science Publishers, 1965, and summarized in THIN FILM PROCESSES, J.L. Vossen, W. Kern, editors, Academic Press, 1978, Part II, Chapter II-1, Glow Discharge Sputter Deposition, both hereby incorporated by reference.

A glow discharge apparatus suitable for batch operation is shown in FIG. 3. In this embodiment, the glow discharge electrode **204** is sufficiently proximate 25 a part **300** (substrate) that the part **300** is an extension of or part of the electrode **204**. Moreover, the part is below a dew point to allow cryocondensation of the glow discharge plasma on the part **300** and thereby coat the part **300** with the monomer condensate and self cure into a polymer layer. Sufficiently proximate 30 may be connected to, resting upon, in direct contact with, or separated by a gap or distance that permits the plasma to impinge upon the substrate. This distance

that the plasma extends from the electrode will depend on the evaporate species, electrode 204/ substrate 104 geometry, electrical voltage and frequency, and pressure in the standard way as described in ELECTRICAL DISCHARGES IN GASSES, F.M. Penning, Gordon and Breach Science Publishers, 1965, hereby incorporated by reference. The substrate 300 may be stationary or moving during cryocondensation. Moving includes rotation and translation and may be employed for controlling the thickness and uniformity of the monomer layer cryocondensed thereon. Because the cryocondensation occurs rapidly, within milli-seconds to seconds, the part may be removed after coating and before it exceeds a coating temperature limit.

In operation, either as a method for plasma enhanced chemical vapor deposition of low vapor pressure materials (coating material) onto a surface, or as a method for making polymer layers (especially PML), the method of the invention has the steps of (a) flash evaporating a coating material monomer forming an evaporate; (b) cryocondensing the evaporate onto a surface and (c) crosslinking the condensed evaporate. The crosslinking may be by radiation, for example e-beam or ultraviolet, by or self curing. Self curing is passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; then cryocondensing the glow discharge monomer plasma on a substrate and crosslinking the glow discharge monomer plasma thereon. The crosslinking results from radicals created in the glow discharge plasma thereby permitting self curing.

The flash evaporating has the steps of flowing a coating material monomer to an inlet, atomizing the material through a nozzle and creating a plurality of monomer droplets of the monomer liquid as a spray. The spray is directed onto a heated evaporation surface whereupon it is evaporated and discharged through an evaporate outlet.

The coating material may be any liquid monomer. However, it is preferred that the liquid monomer or liquid have a low vapor pressure at ambient temperatures so that it will readily cryocondense. Preferably, the vapor pressure of the liquid monomer material is less than about 10 torr at 83 °F (28.3 °C), more preferably less than about 1 torr at 83 °F (28.3 °C), and most preferably less than

about 10 millitorr at 83 °F (28.3 °C). Liquid monomer includes but is not limited to phenylacetylene (**FIG. 1c**), (meth)acrylate and combinations thereof.

When the monomer includes particles, the particle(s) may be any insoluble or partially insoluble particle type having a boiling point below a 5 temperature of the heated surface in the flash evaporation process. Insoluble particle includes but is not limited to phenyl acetylene, triphenyl diamine derivitive (TPD, **FIG. 1d**), quinacridone (QA, **FIG. 1e**) and combinations thereof.

By using flash evaporation, the coating material monomer is vaporized so quickly that reactions that generally occur from heating a liquid material to an 10 evaporation temperature simply do not occur. Further, control of the rate of evaporate delivery is strictly controlled by the rate of material delivery to the inlet **118** of the flash evaporator **106**.

In the embodiment with a glow discharge electrode, additional gases may be added within the flash evaporator **106** through a gas inlet **130** upstream 15 of the evaporate outlet **128**, preferably between the heated surface **124** and the first baffle **126** nearest the heated surface **124**. Additional gases may be organic or inorganic for purposes included but not limited to ballast, reaction and combinations thereof. Ballast refers to providing sufficient molecules to keep the plasma lit in circumstances of low evaporate flow rate. Reaction refers to 20 chemical reaction to form a compound different from the evaporate. Additional gases include but are not limited to group VIII of the periodic table, hydrogen, oxygen, nitrogen, chlorine, bromine, polyatomic gases including for example carbon dioxide, carbon monoxide, water vapor, and combinations thereof.

25 **EXAMPLE 1**

An experiment was conducted to demonstrate the method of the present invention. The monomer was TRPGDA (tri-propylene glycol diacrylate). Several starting conditions were used as indicated in Table E1-1.

Table E1-1 Starting Materials and Amounts

	Sample 1	Sample 2	Sample 3 ^A	Sample 4
Monomer	TRPGDA	TRPGDA	TRPGDA	TRPGDA
TPD (vol%)	10	0	10	0
Alq (vol%)	0	10	10	0
QA	0	0	0	10

^A includes 2 vol% lithium-trifluoromethanesulfonate ($\text{CF}_3\text{SO}_3\text{Li}$)

The monomer particle mixture was flash evaporated under a vacuum of
 5 10-4 torr and condensed upon a substrate of PET moving at a rate between 0 –
 100 ft/min. Curing was by UV, e-beam and self curing by exposure of the
 evaporate to a plasma prior to condensation.

CLOSURE

10

While a preferred embodiment of the present invention has been shown
 and described, it will be apparent to those skilled in the art that many changes
 and modifications may be made without departing from the invention in its
 broader aspects. The appended claims are therefore intended to cover all such
 changes and modifications as fall within the true spirit and scope of the invention.
 15

I claim:

1. A method of making a polymer composite of a molecularly doped polymer, the method comprising the steps of:
 - (a) mixing a liquid monomer with light emitting particles substantially insoluble in the liquid monomer forming a monomer particle mixture, said particles having light emitting molecules;
 - (b) flash evaporating the monomer particle mixture forming a composite vapor; and
 - (c) continuously cryocondensing the composite vapor on a cool substrate and cross linking a cryocondensed monomer layer thereby forming the composite polymer layer of said molecularly doped polymer.
- 15 2. The method as recited in claim 1, wherein flash evaporating comprises the steps of:
 - (a) supplying a continuous liquid flow of said monomer particle mixture into a vacuum environment at a temperature below both the decomposition temperature and the polymerization temperature of the monomer particle mixture;
 - (b) continuously atomizing the monomer particle mixture into a continuous flow of droplets;
 - (c) continuously vaporizing the droplets by continuously contacting the droplets on a heated surface having a temperature at or above a boiling point of the liquid monomer and of the particles, but below a pyrolysis temperature, forming said composite vapor.
- 30 3. The method as recited in claim 1, wherein said cross linking is radiation cross linking.

4. The method as recited in claim 1, further comprising the step of passing the composite vapor past a glow discharge electrode prior to cryocondensing, wherein said cross linking is self curing.

5 5. The method as recited in claim 1, wherein the liquid monomer is selected from the group consisting of (meth)acrylate monomers and combinations thereof.

10 6. The method as recited in claim 5, wherein acrylate monomer is selected from the group consisting of tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate, caprolactone acrylate, and combinations thereof.

15 7. The method as recited in claim 1, wherein the light emitting particles are selected from the group consisting of organic solids, liquids, and combinations thereof.

20 8. The method as recited in claim 7, wherein the organic solids are selected from the group consisting of aluminum quinolinolato, triphynyl diamine derivative, quinacridone, and combinations thereof.

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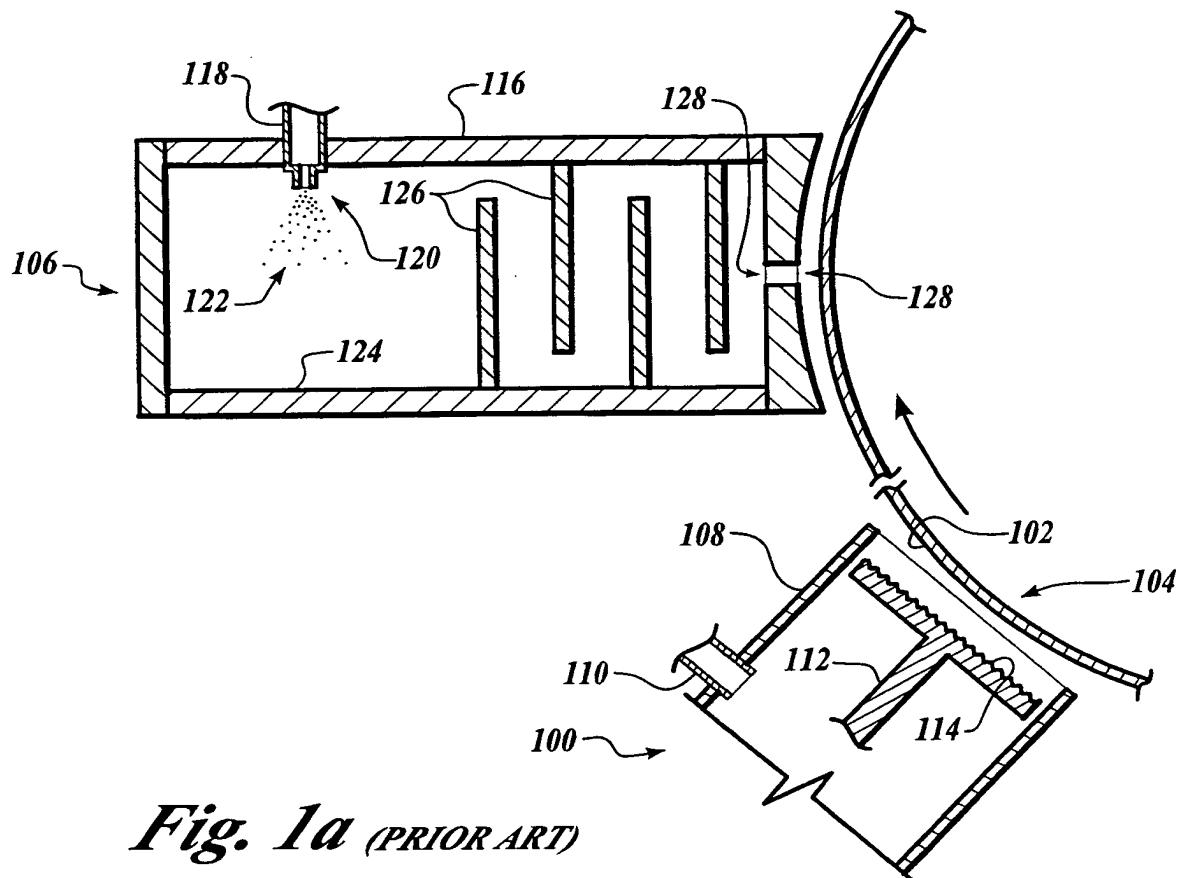


Fig. 1a (PRIOR ART)

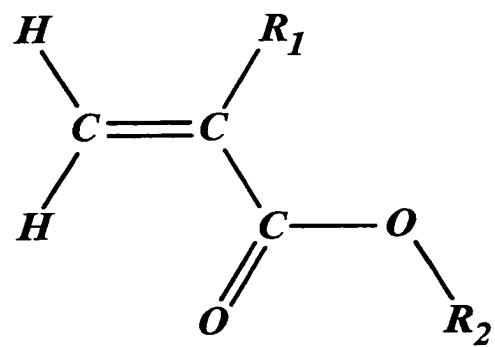
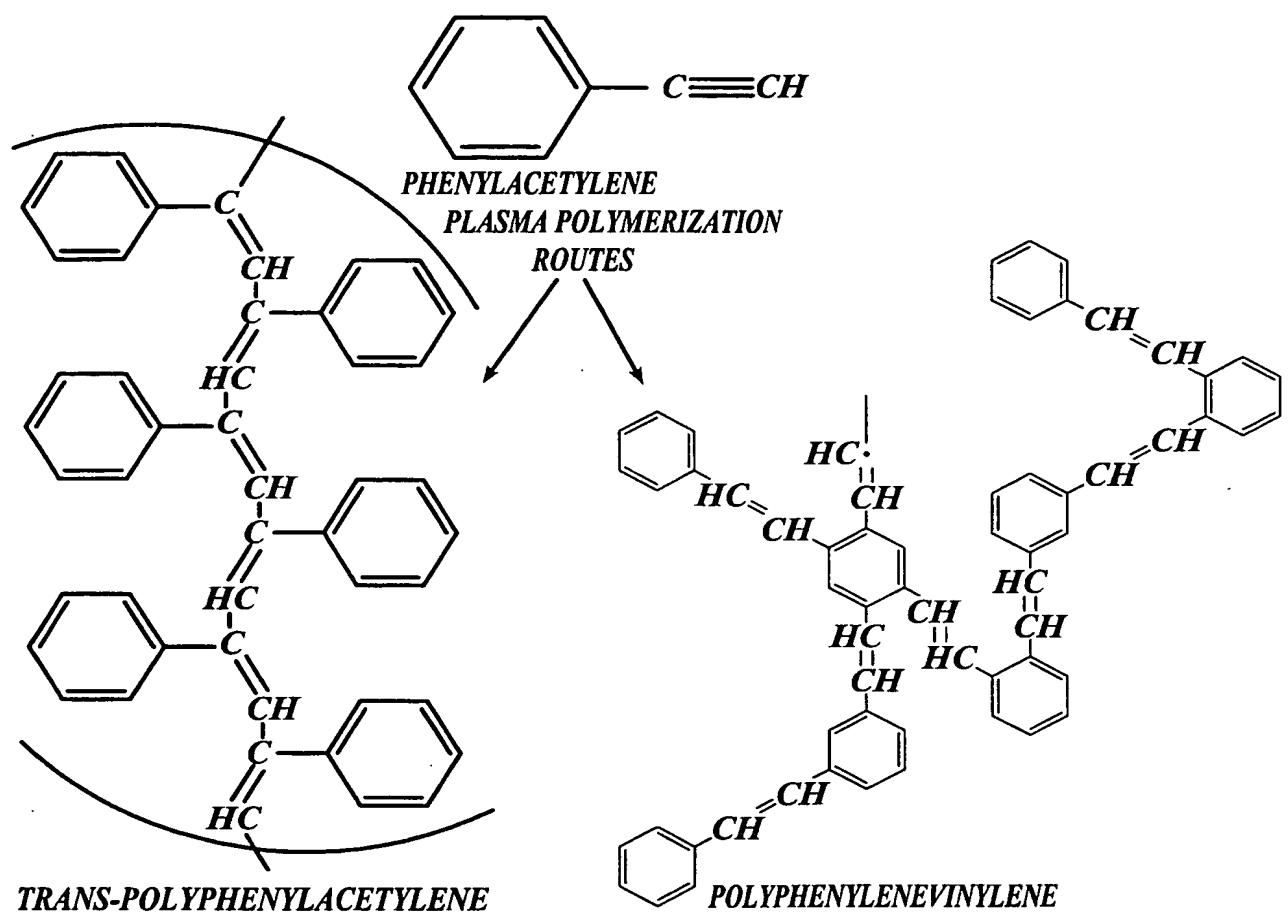
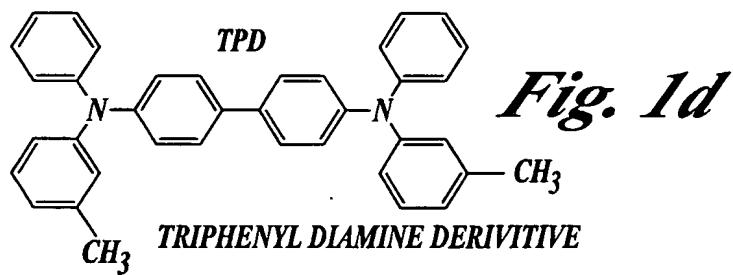
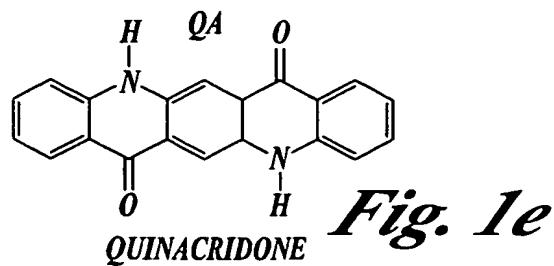
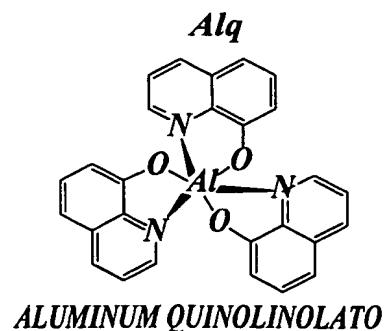
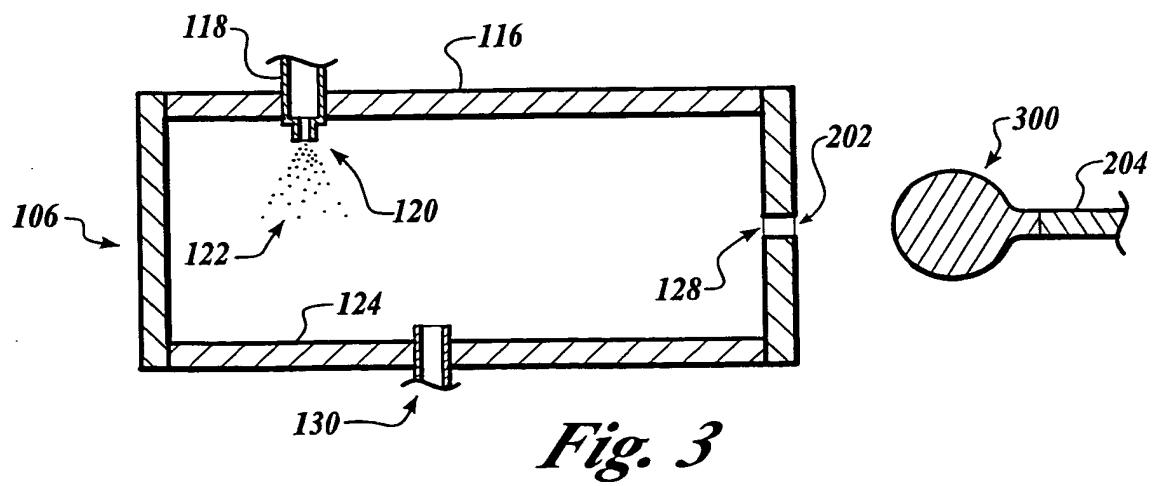
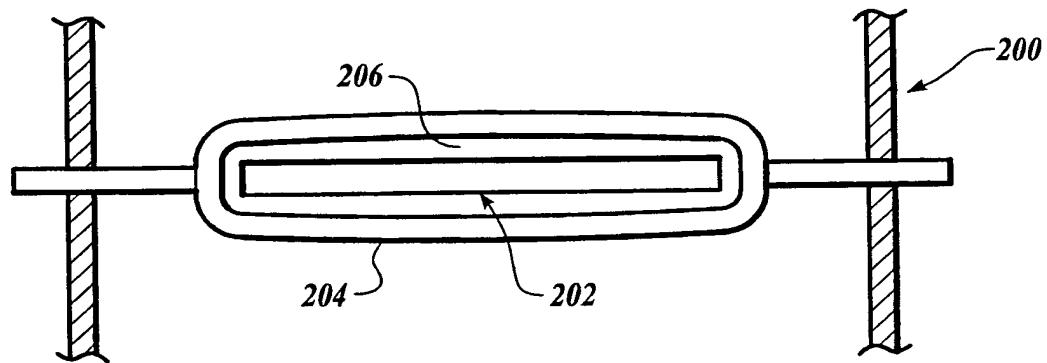
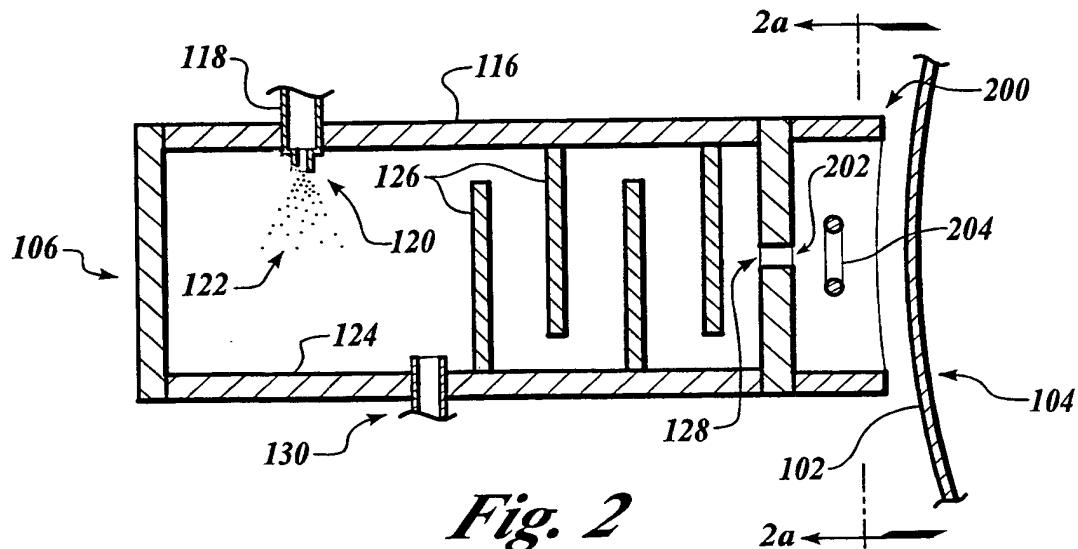


Fig. 1b (PRIOR ART)

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*Fig. 1c**Fig. 1d**Fig. 1e**Fig. 1f*

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/29844

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B05D7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 99 16557 A (BATTELLE MEMORIAL INSTITUTE) 8 April 1999 (1999-04-08) page 4, line 34 -page 6, line 28 ---	1-8
A	WO 97 04885 A (BATTELLE MEMORIAL INSTITUTE) 13 February 1997 (1997-02-13) the whole document ---	1-6
P, A	WO 99 16931 A (BATTELLE MEMORIAL INSTITUTE) 8 April 1999 (1999-04-08) the whole document ---	4
A	WO 98 10116 A (TALISON RESEARCH) 12 March 1998 (1998-03-12) the whole document -----	4

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

^a Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

Date of mailing of the international search report

28 April 2000

09/05/2000

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/29844

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9916557 A	08-04-1999	US	5902641 A	11-05-1999
WO 9704885 A	13-02-1997	US	5681615 A	28-10-1997
		CA	2226496 A	13-02-1997
		CN	1198109 A	04-11-1998
		EP	0843599 A	27-05-1998
		JP	11506045 T	02-06-1999
WO 9916931 A	08-04-1999	NONE		
WO 9810116 A	12-03-1998	NONE		